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PREPARATION OF HOMOGENEOUS 'LIVING' POLYVINYL GELS WITH APPLICA--FTC(U)  
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Preparation of Homogeneous 'Living' Polyvinyl Gels  
with Application to Solvent Purification

by

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ABSTRACT

A method is presented for maintaining a high level of purity in organic solvents to be used in anionic polymerizations. The development of this technique has entailed synthesis of structurally unique polyvinyl gels which are labile to anionic initiation. Preparation of macroscopic homogeneous gels from divinylbenzene (DVB) and ethylstyrene (ES) is shown to result in the immobilization of a significant amount of residual vinyl groups. Conditions necessary for eliminating unwanted syneresis during the gelation include initiation of the reaction with butyllithium and polymerization in a nonpolar solvent (e.g. benzene) to which an appropriate amount of tetrahydrofuran (THF) has been added. The success of this method in obtaining the desired product is attributed to the influence of the THF on the polymerization of DVB; a mechanism is proposed and experimentally supported which accounts for the observed results.

## INTRODUCTION

Recent research objectives in our laboratory have required anionic synthesis of relatively large amounts of well defined, high molecular weight polymers. The standard methods for purifying solvents for these polymerizations involve exhaustive distillation from compounds capable of reacting with deleterious impurities (1,2). Such techniques were not efficient for handling the large quantities of solvents dictated by our synthesis requirements. Therefore, we postulated the following method of establishing and maintaining purity in solvents to be later used in anionic polymerizations. A quantity of gel particles containing immobilized anionically reactive vinyl groups is suspended in the solvent to be purified. Sufficient anionic initiator is added to the point at which gel vinyl group initiation takes place. Prior to gel 'activation', homogeneous reaction between initiator and impurities in the solvent neutralizes any compounds poisonous to an anionic polymerization. Excess initiator is then heterogeneously scrubbed from the solvent by the available sites in the gel. These activated gels further provide a bed of anion 'inertia' capable of maintaining an absolute degree of purity over long periods of time. In the particular case of chromophorically activated gels, the presence of a known color serves as an indicator of gel activity and solvent purity. Purified solvent can simply be drained from the vessel leaving the gel material behind.

This separation scheme requires a polymer gel meeting two criteria. First, it must contain a significant quantity of residual vinyl groups both chemically labile to and physically available for anionic reaction.

Second, such a gel must be structurally sound and easy to handle in order to facilitate its use in solvent purification steps.

A suitable monomer for developing the necessary polyvinyl gel is divinylbenzene (DVB). It can be polymerized either anionically (3,4,5) or by free radicals (6) into a gel. Funke (6) has demonstrated the existence and possible use of residual vinyl groups in such a gel. Although the concentration and availability for reaction of residual active sites is expected to be small, these previously reported gels could in theory satisfy our first material requirement. The second criterion presents a greater problem. All reported methods of DVB gelation are subject to syneresis. This results in a product which is either a microgel (particles which are less than 10 microns in size) or a chalky precipitate with no mechanical integrity (3,4,6). These structural features have limited the chemical and physical application of such materials to a "microregime", e.g. as multifunctional initiators for star block polymers (3,4), in paint formulations (6) or as column packing for gel permeation chromatography.

In this paper we report on the successful polymerization of DVB into a homogeneous gel containing a significant concentration of residual vinyl groups. Our method of synthesis places no restrictions on overall sample size and results in a material of substantial mechanical strength. The utility of these novel polyvinyl macrogels is demonstrated in solvent purification.

#### EXPERIMENTAL

Materials. Divinylbenzene (Matheson, Coleman, Bell practical grade)

was deinhibited by successive washing with 10% NaOH followed by distilled water and was stored over molecular sieves at 0° C. Proton NMR analysis confirmed a monomer composition of 60% DVB and 40% ethyl styrene (ES). The ratio of meta to para DVB was reported as 3 to 1 by the manufacturer. Reagent grade benzene, tetrahydrofuran, 1,4 dioxane, and toluene were dried over molecular sieves. Normal and secondary butyllithium were diluted in hexane or used as received from Aldrich; concentrations were verified by titration using the method of Eppley and Dixon (7).

Reaction Procedure. Reactions were performed at room temperature in sealed, flamed, and argon-flushed pyrex test tubes. Solvents and monomer were each introduced to the vessel by syringe and mixed. Similar addition of initiator was followed by a color change from colorless to burgundy-brown and subsequent gelation. The reacting solution/gel was left for 24 hours and recovered in benzene. Over a period of time, reaction with oxygen terminated the living gels as indicated by loss of color.

Results of gel synthesis in benzene/THF. Varying the molar ratio of THF to initiator between values of  $[THF]/[I] = 0$  and 4 in benzene has a dramatic effect on the product obtained. Initiation in the absence of THF leads to slow development of color with subsequent polymerization and gelation dominated by extensive syneresis; the opaque gel so produced has little mechanical strength and crumbles upon handling. Addition of initiator to a solution with  $[THF]/[I] = 4$  instantaneously produces a burgundy color followed by rapid homogeneous gelation. The product is a clear uniform gel of superior strength. Varying  $[THF]/[I]$  between 0 and 4 results in large changes in reaction time and product characteristics. The polyvinyl macrogel

synthesized with  $[\text{THF}]/[\text{I}] = 4$  was found to provide the most suitable material for application to solvent purification. It can be readily cut into serviceable pieces as recovered in the swollen state, while also containing a sufficient concentration of vinyl groups. The conditions for the synthesis of this gel are summarized in Table 1. Unless otherwise stated, further remarks will refer to this material.

Characterization. The gel was analyzed for accessible vinyl content in the following manner: 1.5 grams (dry weight) of  $0.5 \text{ cm}^3$  size particles were suspended in toluene, charged with excess  $n \text{ BuLi}$  and allowed to react under purified argon for one week. The presence of available vinyl groups for reaction in the gels was evidenced by the appearance of a deep reddish-brown color. The solution was then drained and a 250 ml aliquot of a standardized solution of toluene and benzoic acid was added. The activated gel particles turned colorless. Aliquots (50 ml each) of the remaining solution were titrated for benzoic acid content with a standardized solution of methanol and sodium methoxide. Phenolphthalien was added as an end point indicator. The titration technique was verified independently on a known solution of benzoic acid in toluene. This method yielded results which indicated that at least 30% of the theoretical number of vinyl groups that would be present if no crosslinking had occurred were still present in the final product and were available for reaction. Since extensive crosslinking did occur, the actual percentage is higher. A value of 30% corresponds to  $1.4 \times 10^{-3}$  moles of available vinyl groups per gram of gel.

The method of characterization was chosen in order to duplicate actual conditions employed during solvent purification as discussed in the follow-



ing section. Presumably the true vinyl content is somewhat higher since this chemical reaction is expected to be strongly diffusion limited.

#### APPLICATION

The polyvinyl gel was tested for solvent purification capabilities in a series of anionic polymerizations. Approximately 2.0 grams (dry weight) of gel material were suspended over 1500 ml of predistilled solvent under argon. For the case of polymerizations to be later initiated with *n* butyllithium, a suitable amount of anisole was added to the solvent to provide for a high rate of initiation (8).

Sufficient *n* BuLi (1.6 M) was added to the solvent and the solution was stirred for several days. Sequential lowering of clear gel particles into the solvent provided fresh vinyl material for initiator removal as evidenced by the appearance of a reddish-brown color in the gel. When the newly added gel particles remained colorless the purification of the solvent was assumed to be complete. Gas chromatographic analysis confirmed the purity of the solvent and in particular verified the absence of DVB at a sensitivity of less than 1 part per million.

Styrene and butadiene monomers were purified by conventional methods (9,10). Diluted solutions of normal and secondary butyllithium in hexane were titrated as previously mentioned (7). All polymerizations were carried out under purified argon.

After introducing the purified solvent to the reactor leaving the activated gels behind, a metered amount of monomer was added and initiated with butyllithium. The amount of monomer varied between 33 and 50 grams.

Reaction temperatures ranged from 30 to 50° C. Upon completion of the reaction, the 'living' polymer was terminated with a small amount of alcohol.

The polymers were analyzed by high performance size exclusion chromatography (HPSEC) (11) employing a set of Zorbax PSM bimodal columns with THF as the mobile phase. Table 2 compares the experimentally obtained number average molecular weight of each sample to that predicted by the stoichiometry of initiator and monomer charged to the reactor. Deviations of actual to theoretical molecular weight are well within the limitations set by the accuracy of our equipment. Low polydispersity indices were also obtained as expected and are listed in table 2.

A polymerization under similar conditions with solvent prepared in an identical fashion except for the gel purification resulted in complete deactivation of added initiator and no polymerization. This clearly illustrates the capabilities of the polyvinyl gel material in this solvent purification application.

It should also be noted that the counterion utilized in solvent purification can be matched with that used during polymer synthesis thereby eliminating difficulties which might arise due to counter-ion exchange. Proper selection of reaction conditions may also allow for gel synthesis in a variety of solvents, the choice depending upon the eventual application. This point will be clarified in the discussion section.

A potential complication of this method of solvent purification is the presence of products (e.g. alkoxides) of the reaction between initiator and impurities in the solvents. Under many conditions (diene polymerization being one possible exception) such byproducts have no detrimental influence on the polymerization. Furthermore sufficient gel activation should provide an adequate number of living sites to bind these complexing compounds which

otherwise would be destined to remain in solution. However, to test the possible influence of these byproducts, NMR analysis of the polybutadiene sample listed in Table 2 was carried out. This experiment identified a microstructure composed of 87% 1,4 (cis and trans) and 13% 1,2 addition. This is consistent with previously documented values for lithium catalyzed anionic polybutadiene prepared in non-polar solvents using conventional methods of purification.

The major advantages of this technique of solvent purification can be summarized as follows:

- (a) Simple establishment, maintenance and verification of an absolute level of purity in organic solvents to be used in anionic polymerizations.
- (b) Avoidance of tedious and energy inefficient separation schemes.
- (c) Direct applicability to large scale polymerizations involving sizeable quantities of solvents.

#### DISCUSSION

The unfavorable structural characteristics of DVB gels prepared in the absence of THF can be attributed to the occurrence of syneresis. Inter- and intra-chain pendant vinyl group polymerization results in local precipitation, and further reaction is limited by monomer diffusion. Subsequent monomer and residual pendant vinyl group polymerization ties this suspension into a heterogeneous network. An analogous situation develops when DVB is emulsion polymerized although the product is recovered as a microgel (6).

Addition of THF at a molar concentration of four times that of initiator has several effects. The rate of initiation and polymerization are both

greatly enhanced as evidenced by the time required to develop full color and gel. This is not surprising since polar materials are known to exert a large influence on the rate of organolithium reactions in hydrocarbon solvents (10). Unexpectedly, THF also suppresses syneresis, thereby permitting preparation of macroscopic homogeneous gels.

We have found that gels initiated with secondary butyllithium in the absence of THF exhibit even less structural integrity than those obtained under similar conditions using n butyllithium. This is due to the development of more extensive syneresis prior to macroscopic gelation. Thus, it is clear that simply increasing the rate of initiation (i.e. by using secondary rather than normal butyllithium) relative to the rate of polymerization induces undesirable effects. Therefore, although it also increases the rate of initiation, the major contribution of THF in our reactions must be attributed to its influence on the mechanism of propagation.

We believe that in the presence of THF the monomer is substantially converted into soluble linear polymer prior to crosslinking. Subsequent reaction of pendant vinyl groups produces the macroscopic homogeneous network observed. Each crosslink step increases the functionality of the living site, thereby decreasing its availability for further reaction. In the absence of monomer, the anions become effectively immobilized and can not polymerize away from the crosslink site.

The homogeneous living gels described here in fact remain clear and exude no solvent over a period of many days. Recovery in pure solvent produces no additional swelling. Lowering the concentration of monomer by a factor of four (to 5% by volume) has no effect on the clarity of the final product nor on the time dependent stability of the gel. Under these conditions the reaction goes to completion at a proportionately higher swelling

ratio. Although we have no explanation for this phenomenon, cessation of crosslinking apparently corresponds to the point of swelling equilibrium. Drying and weighing recovered gels has verified complete conversion of monomer to polymer. Furthermore, upon solvent removal and annealing, isotropic shrinkage accounts for essentially all of the volume previously occupied by solvent. These observations appear to be consistent with the proposed sequence of events leading to homogeneous gelation and anion immobilization.

How then does THF affect the mechanism of polymerization which leads to the observed suppression of syneresis? Examination of the literature provides the following information about the relative susceptibility of meta and para DVB to organolithium reaction.

(a) In benzene containing 2% THF the first double bond of para DVB reacts ten times faster than the second. Also, the reactivity of the second double bond is equal to that of styrene (12).

(b) In pure benzene the reactivity of the two double bonds of para DVB differ significantly (13).

(c) The two double bonds of meta DVB are equally reactive in pure benzene (13).

The higher reactivity of para DVB monomer can be attributed to the conjugated nature of the vinyl groups which is lost upon polymerization through the first double bond. No such enhancement is present for meta DVB. On these grounds the presence of THF should have no effect on the ratio of the reactivities of the first and second double bonds of para DVB. As indicated by (a) and (b) this appears to be experimentally borne out. By the same reasoning the THF is not expected to change the relative

reactivities of the double bonds of meta DVB which is present in three fold excess over para DVB in our reactions. Based on this information one would expect no structural variations to be found in gels produced with or without THF. However, this reasoning is based solely on considerations of relative nucleophilicity. Reaction rates may also be strongly influenced by entropic (frequency factor) effects.

To facilitate the discussion we assume that the mechanisms of propagation for the monomers employed correspond to those of styrene monomer in the respective solvents. This seems reasonable based on nucleophilic and steric similarities. At the concentration of THF employed here, propagation is expected to proceed predominantly via solvated monoetherates of living lithium poly(divinylbenzene-ethylstyrene)(10). In the absence of THF an equilibrium is established between dimeric lithium poly (divinylbenzene-ethylstyrene) and the monomeric species, the latter providing the predominant path for vinyl addition. Estimates of the equilibrium constant of this association indicate that the bulk of the growing chains are in the associated state (10). We believe that it is this association that leads to syneresis in the case of gel reactions in benzene and furthermore that elimination of the association in various ways can explain homogeneous gels of the type described above.

For the case of dimeric lithium poly (DVB-ES), as found in benzene without THF, the close proximity afforded the terminal pendant vinyl group of one living chain to the active end of its associated counterpart greatly enhances the probability of inter-chain reaction upon dissociation. This will double the molecular weight and functionality of the resulting species. Furthermore, reassociation with the original partner becomes sterically

impossible until further reaction relieves such steric restrictions. Successive dimerization and crosslinking with separate species will quickly increase the molecular weight, the crosslink density and the functionality of the living polymer leading to syneresis. This scenario is consistent with all of our experimental observations for reactions in benzene (also for reactions in toluene not described in detail here).

Addition of THF to the benzene solvent has two important effects. First the presence of THF eliminates the possibility of living end associations; unassociated monoetherates are the predominant living species present in benzene/THF solvent at the concentrations of THF employed here (10). Second the mechanism of propagation in the presence of THF is dramatically changed so that vinyl addition occurs via a coordinated vinyl-monoetherate complex (10). We believe that it is only the first of these two effects which leads to the suppression of syneresis in our gelation reactions leading to the production of homogeneous gels.

In order to examine this hypothesis in more detail we have performed a series of gelation reactions in a mixed solvent composed of 75% dioxane and 25% toluene (v/v). It has been shown that lithium polystyryl in dioxane exists as and propagates via unassociated contact ion pairs (10). Therefore by carrying out a gelation in this solvent we have maintained the same addition mechanism as for the case of benzene while eliminating the undesirable living end association. The 25% toluene was added to the dioxane in order to obtain a solubility parameter comparable to that of benzene while leaving the dielectric characteristics of the solvent mixture for the most part unchanged from that of pure dioxane.

The results of these experiments are indicated in Table 3 along with the corresponding information from the previous two cases. As expected, the clarity and structural characteristics of the dioxane/toluene and benzene/THF gels were indistinguishable. Furthermore, the trend observed in the times to gelation is consistent with the reported (10) values for the rates of polymerization of styrene in the respective solvents (Table 3). This supports our previous assumption about the similarity in reaction mechanisms between that of divinylbenzene-ethyl styrene and of styrene.

Thus, the dominant factor in suppressing syneresis is the avoidance of lithium poly (DVB-ES) dimerization. This favorable condition can be achieved in a variety of ways, for example, by the addition of small amounts of THF (1,2 dimethoxyethane has also been shown to work) to solvents such as benzene, or by the selection of appropriate overall solvent mixture such as dioxane/toluene. In the absence of such association early stage polymerization is expected to be predominantly linear chain growth due to the high concentration of monomer units relative to polymer repeat units. Linear polymerization is also enhanced by a degeneracy of two between the vinyl content of DVB monomer versus polymer repeat unit along with the inability of ethylstyrene to contribute to crosslinking. Polymer chain diffusional and steric restrictions may also favor linear addition although this is difficult to prove. Nonetheless, prior to gelation, the reaction medium is composed of soluble living polymer which then forms a stable macroscopic homogeneous network. The utility of these novel materials has been demonstrated for the particular case of purification of solvent. Numerous other applications can be envisioned.



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TABLE 1

Reagent	Concentration (mole/liter)
DVB (75% meta, 25% para)	0.83
Ethylstyrene (mixed isomers)	0.55
Benzene	9.01
n-BuLi	0.016
THF	0.064

Experimental conditions for the synthesis of gels used in solvent purification.

TABLE 2

Monomer	Solvent	$M_N^{(a)}$ theoretical	$M_N^{(b)}$ experimental	$M_w/M_N^{(b)}$
styrene	toluene <sup>(c)</sup>	99,000	105,000	1.19 <sup>(d)</sup>
styrene	benzene <sup>(e)</sup>	81,000	81,000	1.06
styrene	benzene <sup>(e)</sup>	149,000	144,000	1.06
butadiene	benzene <sup>(e)</sup>	90,000	94,000 <sup>(f)</sup>	1.05 <sup>(f)</sup>

Comparison of theoretical and actual molecular weights obtained for polymerization of listed monomers in solvent purified using polyvinyl gels.

(a) Determined by stoichiometry of monomer and initiator charged to the reactor

(b) Determined by HPSEC calibrated with 10 polystyrene standards

(c) Initiated with sec butyllithium

(d) This relatively high value is expected due to chain transfer reaction (14)

(e) Initiated with n butyllithium in the presence of anisole

(f) Calculated using universal calibration with data from ref. 15

TABLE 3

Solvent	Benzene	Benzene/THF (0.994/0.006)	Dioxane/Toluene (0.750/0.250)
time to full color (sec)	>120	instantaneous	instantaneous
time to gel (sec) <sup>(a)</sup>	~1200	~20	~160
expected overall rate constant (liter mole <sup>-1</sup> sec <sup>-1</sup> ) <sup>(b)</sup>	0.01	25.3 <sup>(c)</sup>	0.9
clarity of gel	opaque	clear	clear
structural characteristics of gel	inhomogeneous (powder)	homogeneous (swollen rubber)	homogeneous (swollen rubber)

Variations observed in gelation reactions and products. Experimental conditions are as in Table 1 keeping the relative volume of solvent constant.

(a) Subject to small deviations due to an inability to accurately control reaction temperature.

(b) Based on values for lithium polystyryl (from ref. 10).

(c) Assuming propagation is via monoetherate of lithium poly (DVB-ES) (from ref. 10).

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